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## Formation and Properties of Bis(borane)alkanethiolate Salts and Their Conversion into *µ*-Alkylthiodiboranes

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Summary Stoicheiometric quantities of KSR and B<sub>2</sub>H<sub>6</sub> react in THF to form the thermally stable salts K[RS- $(BH_3)_2$ ; treatment of  $K[RS(BH_3)_2]$  with anhydrous acids, diborane, or iodine produces  $\mu$ -RSB<sub>2</sub>H<sub>5</sub> in moderate yield.

RELATIVELY little is known about sulphur substituted boranes and borohydride ions. We report the extension of earlier work 1-3 to the preparation and characterization of a number of new S-alkyl substituted compounds.

$$MSR + B_2H_6 \longrightarrow M[RS(BH_3)_2]$$
(1)

The preparation equation (1) and characterization of  $K[EtS(BH_3)_2]$  is typical. Treatment of a stirred THF slurry of KSEt with an exact stoicheiometric quantity of  $B_2H_6$  results in rapid dissolution of the solid. Evaporation gives pure solvent-free  $K[EtS(BH_3)_2]$ ; no  $KBH_4$  or (EtSBH<sub>2</sub>), forms under these conditions. K[EtS(BH<sub>3</sub>)<sub>2</sub>] dissolves in glyme ethers and THF, but reacts with protic solvents. The boron-11 n.m.r. spectrum<sup>†</sup> (THF) consists of a quartet at 22.6 p.p.m., J 97 Hz; the i.r. spectrum shows the following bands in the B-H stretching region (in cm<sup>-1</sup>): 2375, (s, sh), 2330 (s), 2295 (s), and 2202 (m).  $K[EtS(BH_3)_2]$  is indefinitely stable at room temperature in the absence of air and moisture and decomposes smoothly at  $80^{\circ}$  in agreement with equation (2).

$$K[EtS(BH_3)_2] \xrightarrow{80^{\circ}} KBH_4 + \frac{1}{s}(EtSBH_2)_s$$
(2)

The thermal stability of  $K[EtS(BH_3)_2]$  stands in contrast to the behaviour of  $[{\rm Et}_4{\rm N}][{\rm HS}({\rm BH}_3)_2],$  which decomposes vigorously with loss of hydrogen above  $-78^{\circ.4}$  The instability of the latter probably results from the acidic proton on sulphur.

Conversion of K[EtS(BH<sub>3</sub>)<sub>2</sub>] into  $\mu$ -EtSB<sub>2</sub>H<sub>5</sub> may be effected as shown in equations (3)—(5).

$$\begin{array}{l} \text{K}[\text{EtS}(\text{BH}_3)_2] + \text{HX} \longrightarrow \text{H}_2 + \text{KX} + \mu\text{-EtSB}_2\text{H}_5 \\ \text{HX} = \text{HCl}, \text{H}_2\text{SO}_4, (\text{HPO}_3)_x \end{array}$$
(3)

$$\begin{array}{c} \text{xylene} \\ \text{K[EtS(BH_3)_2]} + \frac{1}{2}\text{B}_2\text{H}_6 \xrightarrow{} \mu \text{-EtSB}_2\text{H}_6 + \text{KBH}_4 \end{array}$$
(4)

toluene

 $K[EtS(BH_3)_2] + \frac{1}{2}I_2 \longrightarrow \mu - EtSB_2H_5 + KI + \frac{1}{2}H_2$ (5)

Decomposition of  $\mu$ -EtSB<sub>2</sub>H<sub>5</sub> at 25° occurs slowly in the gas phase and rapidly in the liquid phase in accord with equation (6).

$$\mu\text{-EtSB}_{2}H_{5} \longrightarrow \frac{1}{2}B_{2}H_{6} + \frac{1}{n}(\text{EtSBH}_{2})_{n}$$
(6)

Reactions (3) and (4) are convenient methods for the preparation of free  $\mu$ -EtSB<sub>2</sub>H<sub>5</sub>; the product may be isolated in 20-30% yield by trap to trap vacuum line fractionation. Reaction (5) is most suitable for the preparation of a toluene solution of  $\mu$ -EtSB<sub>2</sub>H<sub>5</sub>. In this case yields are generally much higher, since isolation of liquid  $\mu$ -EtSB<sub>2</sub>H<sub>5</sub> and resultant accelerated decomposition are avoided.

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† The boron-11 n.m.r. spectra were obtained using a Varian HA-100 spectrometer equipped with a 32·1 MHz probe. Chemical shifts are relative to Et<sub>2</sub>O,BF<sub>3</sub>.

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